

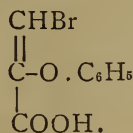
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LI.—ON MUCOXYBROMIC AND MUCOXYCHLORIC ACIDS.¹

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The action of baric hydrate upon mucobromic acid was studied several years ago by O. R. Jackson and one of us.² It was found that mucobromic acid was decomposed by a large excess of baric hydrate with the formation of $\alpha\beta$ dibromacrylic and formic acids, while an essentially different reaction ensued in a feebly alkaline solution. The main product in this case was shown to be a dibasic acid containing four atoms of carbon; but it was not further studied. Somewhat later, E. K. Stevens and one of us³ found that mucophenoxybromic acid was formed by an analogous reaction when mucobromic acid was treated with potassic phenylate; and the constitution of this acid was established with little difficulty by its conversion into phenoxybrommaleic and phenoxybromacrylic acids. The great stability of the latter acid in alkaline solution left no doubt that its structure was represented by the formula



¹ From the Proceedings of the American Academy of Arts and Sciences. Communicated by the authors.

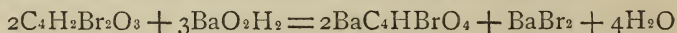
² Proceedings American Academy 16, 188.

³ This Journal 6, 187; and Proceedings 19, 262.

While it was thus rendered probable that in the corresponding decompositions by baric hydrate an atom of bromine in the mucobromic acid had been replaced by hydroxyl, and the empirical formula of the product formed also warranted this conclusion, it was difficult to obtain any definite experimental evidence in its support. The isomerism of this acid with monobrommaleic and monobromfumaric acid, and its strongly marked dibasic character, made its constitution a question of decided interest. We therefore undertook its more extended investigation, as well as a study of the analogous chlorine compound, which could readily be obtained from mucochloric acid. Although our investigations are in many respects incomplete, they seem to us to leave little doubt as to the constitution of the compounds in question; and since we shall be unable to continue the work together, we have thought it best to present the results which we have already obtained.

Mucoxybromic Acid.

Whenever mucobromic acid is dissolved in a solution of an alkaline hydrate, more or less mucoxybromic acid appears to be formed. For its preparation, however, we have found it necessary to use baric hydrate, and the yield is then largely dependent upon the conditions under which the reaction takes place. We have found it most advantageous to suspend the mucobromic acid in thirty parts of cold water, and, after cooling well with ice, to add gradually, with constant shaking, finely powdered baric hydrate of known strength. After the mucobromic acid is neutralised, the baric hydrate must be added in small quantities, and the solution allowed to stand until the alkaline reaction has nearly disappeared before a fresh portion is added. The alkaline reaction disappears rapidly at first, afterwards more slowly, and when the amount of baric hydrate demanded by the equation



has been added, the reaction usually remains feebly alkaline, even after long standing. The slight excess of baric hydrate is then removed by carbonic dioxide, and an equal volume of alcohol added to the filtered solution. Baric mucoxybromate, which is very sparingly soluble in dilute alcohol, is thus precipitated in the form of fine, flattened, pointed needles, and may be purified by dissolving in cold water and reprecipitating with alcohol. With

careful work, about sixty per cent. of the theoretical yield may be obtained. The preparation of the free acid from the barium salt is a matter of considerable difficulty, since it cannot be extracted from aqueous solution by the ordinary solvents, and it is quickly decomposed during the evaporation of its solution, even at ordinary temperatures. We succeeded in preparing it only by moistening the salt with a little water, precipitating the barium exactly with sulphuric acid, and evaporating the concentrated solution of the acid thus obtained as rapidly as possible over sulphuric acid in vacuo. The viscous residue thus obtained gradually solidified at low temperatures, and yielded tolerably well-formed thick prisms with beveled ends. The substance, freed from the viscous mother liquors as completely as possible and dried over sulphuric acid, gave, on analysis, the following results:

I. 0.7181 gram substance gave 0.6451 gram CO_2 and 0.1004 gram H_2O .

II. 0.7504 gram substance gave 0.6697 gram CO_2 and 0.1010 gram H_2O .

III. 0.2053 gram substance gave 0.1977 gram AgBr .

IV. 0.2348 gram substance gave 0.2254 gram AgBr .

	Calculated for $\text{C}_4\text{H}_3\text{BrO}_4$.	I.	II.	Found.	
				III.	IV.
C	24.60	24.50	24.34		
H	1.54	1.55	1.50		
Br	41.03	...	...	41.00	40.86

Mucoxybromic acid is extremely soluble in water, alcohol, or ether, and almost insoluble in chloroform, benzol, ligroin, or carbonic disulphide. The melting point was found to be 111° – 112° ; the true melting point may, however, be somewhat higher, since the substance could not be purified by repeated crystallisation. The acid gives with ferric chloride an intense garnet-red coloration, which is readily seen, even in very dilute solutions. With argentic nitrate it gives a white crystalline precipitate of the silver salt. Baric acetate added to a concentrated aqueous solution throws down the highly crystalline barium salt. By the action of hydrobromic acid saturated at 0° , or of phosphoric pentabromide, no definite products were obtained.

Baric Mucoxybromate, $\text{BaC}_4\text{HBrO}_4 \cdot 2\text{H}_2\text{O}$.—The preparation of the barium salt has already been described. The salt is somewhat sparingly soluble in cold water, and its solubility is not sensibly

increased by heat. It is rapidly decomposed by boiling its aqueous solution, and even in the cold decomposition ensues after long standing. On the evaporation of a solution saturated at ordinary temperatures over sulphuric acid in vacuo, the salt separates in long lustrous six-sided prisms with perpendicular terminations. The air-dried salt loses over sulphuric acid, or at 100° , rather more than one molecule of water, and has then the composition $\text{BaC}_4\text{HBrO}_4 \cdot \text{H}_2\text{O}$. When heated to 105° – 115° , it slowly loses the second molecule of water, but at the same time it turns brown, and baric bromide is formed.

I. 1.5527 grams of the salt, crystallised from water and dried by exposure to the air, lost over sulphuric acid 0.0953 gram H_2O .

II. 1.0746 grams of the salt, precipitated by alcohol and dried by exposure to the air, lost over sulphuric acid 0.0663 gram H_2O .

III. 1.0502 grams of the salt, precipitated by alcohol and dried by exposure to the air, lost over sulphuric acid 0.0631 gram H_2O .

	Calculated for $\text{BaC}_4\text{HBrO}_4 \cdot 2\text{H}_2\text{O}$.	I.	Found. II.	III.
H_2O	4.92	6.14	6.17	6.01

The salt dried over sulphuric acid gave, on analysis, the following results:

I. 0.2769 gram of the salt gave 0.1837 gram BaSO_4 .

II. 0.2052 gram of the salt gave 0.1368 gram BaSO_4 .

III. 0.5470 gram of the salt gave 0.3678 gram BaSO_4 .

IV. 0.4128 gram of the salt gave 0.2079 gram CO_2 and 0.0354 gram H_2O .

V. 0.4988 gram of the salt gave 0.2516 gram CO_2 and 0.0477 gram H_2O .

VI. 0.2120 gram of the salt gave 0.1128 gram AgBr .

VII. 0.2684 gram of the salt gave 0.1457 gram AgBr .

	Calculated for $\text{BaC}_4\text{HBrO}_4 \cdot \text{H}_2\text{O}$.	I.	II.	III.	Found. IV.	V.	VI.	VII.
Ba	39.37	39.00	39.19	39.54				
C	13.77	...	...	...	13.74	13.76		
H	0.86	...	...	...	0.95	1.06		
Br	22.99	...	...	...	...	...	22.64	23.11

We have made many unsuccessful attempts to prepare an acid barium salt. In every case, when the acid solution was precipitated with alcohol, or evaporated in vacuo over sulphuric acid, we obtained only the neutral salt.

Potassic Mucoxybromate, $K_2C_4HBrO_4 \cdot H_2O$.—The potassium salt was prepared from the barium salt by exact precipitation with potassic carbonate, and evaporation of the solution thus obtained in vacuo. It crystallised in well-formed rhombic plates, which were very soluble even in cold water. On warming the solution, decomposition quickly ensued. The air-dried salt lost nothing over sulphuric acid, turned somewhat brown at 70° , but did not lose sensibly in weight until heated to 100° .

I. 0.4951 gram of the air-dried salt lost, at 100° , 0.0344 gram H_2O , and gave 0.2991 gram K_2SO_4 .

II. 0.4604 gram of the air-dried salt lost, at 100° , 0.0307 gram H_2O , and gave 0.2780 gram K_2SO_4 .

III. 0.5428 gram of the air-dried salt gave 0.3281 gram K_2SO_4 .

	Calculated for $K_2C_4HBrO_4 \cdot H_2O$.	I.	Found. II.	III.
K	27.04	27.12	27.10	27.14
H_2O	6.64	6.95	6.67	

Argentio Mucoxybromate, $Ag_2C_4HBrO_4$.—Argentio nitrate added to a solution of the free acid, or one of its salts, throws down a crystalline precipitate of the silver salt. When this is warmed with water, argentio bromide is at first formed, then reduction takes place. When heated in a slightly ammoniacal solution, it is immediately blackened. It dissolves readily in dilute nitric acid, but the solution soon grows turbid with the separation of argentio bromide. The dry salt explodes on heating, or on moistening with concentrated nitric acid. For analysis, the salt was made by precipitating an excess of argentio nitrate with a dilute solution of the barium salt.

I. 0.3974 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr , 0.3634 gram $AgBr$.

II. 0.5478 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr , 0.5034 gram $AgBr$.

III. 0.5455 gram of the salt dried in vacuo over H_2SO_4 gave, on precipitation with HBr , 0.4999 gram $AgBr$.

IV. 0.5866 gram of the salt dried in vacuo over H_2SO_4 gave, on heating in sealed tube with diluted nitric acid, 0.2672 gram $AgBr$.

	Calculated for $Ag_2C_4HBrO_4$.	I.	II.	Found. III.	IV.
Ag	52.82	52.53	52.78	52.64	
Br	19.56	...	...	...	19.38

A solution of the barium salt yielded, with plumbic nitrate, a heavy yellow semi-crystalline precipitate, which, when dried over sulphuric acid, gave on analysis percentages of lead and bromine which only approximated those required by the formula $\text{PbC}_4\text{HBrO}_4$.

Dimethyl Mucoxybromate, $\text{C}_4\text{HBrO}_4(\text{CH}_3)_2$.—The dimethyl ether of mucoxybromic acid can readily be formed by the action of methyl iodide upon the dry silver salt. If the methyl iodide is slowly added to the silver salt, so much heat is evolved that a violent and even dangerous explosion ensues. The silver salt must therefore be added in small portions to an excess of methyl iodide, or must be suspended in dry ether before adding the methyl iodide. The product of the reaction proved to be a viscous, sticky liquid, which showed no signs of crystallisation after long standing over sulphuric acid in vacuo, and which could not be volatilised, even in vacuo, without decomposition. The substance dried over sulphuric acid in vacuo for several days gave somewhat too low a percentage of bromine.

0.3653 gram substance gave 0.3031 gram AgBr.

	Calculated for $\text{C}_4\text{HBrO}_4(\text{CH}_3)_2$.	Found.
Br	35.88	35.30

Diethyl Mucoxybromate, $\text{C}_4\text{HBrO}_4(\text{C}_2\text{H}_5)_2$.—This substance we attempted to prepare by the action of ethyl iodide diluted with dry ether upon the silver salt. We obtained a thick viscous product, which we were unable to purify, and which, after long standing over sulphuric acid in vacuo, proved to contain iodine, and gave too high a percentage of halogen.

I. 0.2288 gram substance gave 0.1911 gram AgBr.

II. 0.2328 gram substance gave 0.1920 gram AgBr.

	Calculated for $\text{C}_4\text{HBrO}_4(\text{C}_2\text{H}_5)_2$.	Found.	
Br	31.82	I. 35.56	II. 35.10

The ether was decomposed by an excess of baric hydrate, the excess of baric hydrate precipitated by carbonic dioxide, and alcohol added to the filtrate solution. We obtained in this way a crystalline salt, which possessed all the properties of baric mucoxybromate.

0.5875 gram of the air-dried salt gave 0.3720 gram BaSO_4 .

	Calculated for $\text{BaC}_4\text{HBrO}_4 \cdot 2\text{H}_2\text{O}$.	Found.
Ba	37.43	37.23

Monoethyl Mucoxybromate, $C_4H_7BrO_4 \cdot C_2H_5$.—If ordinary ether is used instead of anhydrous ether in the preparation of the ethyl ether, the acid ether is obtained. We added the dry silver salt slowly to an excess of ethyl iodide, and after the first reaction was over, warmed for a short time on the water-bath. The product was then extracted with ordinary ether, and the ethereal extract allowed to evaporate spontaneously. The syrupy residue thus obtained gradually yielded an abundance of clear prisms with oblique truncations, which were pressed out and recrystallised from boiling benzol.

0.2068 gram of substance dried over H_2SO_4 gave 0.1762 gram AgBr.

	Calculated for $C_4H_7BrO_4 \cdot C_2H_5$.	Found.
Br	35.88	36.25

The monoethyl mucoxybromate dissolves quite readily in water, its solution has a strongly acid reaction, and gives with ferric chloride an intense red coloration. It dissolves readily in alcohol, ether, chloroform, or hot benzol, more sparingly in ligroin or carbonic disulphide. The melting point of the substance repeatedly recrystallised from benzol was found to be 88° – 89° .

Decomposition in Alkaline Solution.

The instability of mucoxybromic acid and its salts in aqueous solution led us to study the reaction more closely, with the hope that the products of this decomposition might throw light upon the constitution of the acid. When a solution of the barium salt is heated to boiling, it soon acquires an acid reaction, and before long grows turbid, with the separation of acid baric oxalate. The reaction then appears to progress slowly, and even after long boiling the decomposition is incomplete. In an alkaline solution, however, complete decomposition is readily effected. Baric hydrate appears to have no action upon mucoxybromic acid in the cold. After standing for days the solution is still clear, and contains no baric bromide. On heating, baric oxalate and baric carbonate are soon thrown down, and in solution may then be found baric bromide and baric formiate. The barium salts which were precipitated on boiling were collected on a filter, and the presence of oxalic and carbonic acids proved by qualitative tests. The oxalic acid was then converted into the calcium salt, and its identity further established by analysis.

0.3141 gram of the salt dried at 100° gave 0.2883 gram CaSO_4 .

Calculated for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

27.39

Found.

27.01

The alkaline solution filtered from the precipitated baric oxalate and carbonate was freed from the excess of baric hydrate by carbonic dioxide, and concentrated by evaporation on the water-bath. It gave with argentic nitrate a heavy precipitate of argentic bromide, and the filtered solution, containing an excess of argentic nitrate, deposited metallic silver on heating. After removing the barium with dilute sulphuric acid, the solution yielded an acid distillate, from which plumbic formiate was obtained by neutralising with plumbic carbonate.

0.2498 gram of the salt dried over H_2SO_4 gave 0.2542 gram PbSO_4 .

Calculated for $\text{Pb}(\text{CHO}_2)_2$.

69.69

Found.

69.50

Beside baric formiate and baric bromide the aqueous solution contained, in small but not insignificant quantity, an amorphous gummy barium salt, whose nature we have been unable to determine, since all our attempts to convert it into a compound fit for analysis have proved unsuccessful. The formation of this gummy barium salt, together with the fact that quantitative determinations of the amounts of carbonic and oxalic acid formed in the reaction showed no simple ratio between the two, leaves little doubt that the reaction is essentially complex in its nature. When an aqueous solution of baric mucoxybromate is boiled with the addition of baric carbonate, the products of the decomposition appear to be the same. The action of water upon the free acid, which is doubtless similar, we have not yet studied in detail.

Action of Bromine in Aqueous Solution.

By the action of most of the ordinary oxidising agents upon mucoxybromic acid or its salts, we were unable to obtain any definite oxidation products except oxalic acid. Bromine water, however, gave us more satisfactory results. On adding bromine slowly to an aqueous solution of the acid, the color of the bromine rapidly disappeared, oxalic acid was formed, and at the same time a well-defined product containing bromine could be isolated. We found that the same reaction ensued, and apparently rather more

neatly, when the barium salt was taken instead of the free acid. Two molecules of bromine were therefore added to a dilute solution of the barium salt. After standing for several hours, the color of the bromine had completely disappeared, and crystals of acid baric oxalate had separated in abundance. The strongly acid solution was then neutralised with calcic carbonate, filtered, and extracted with ether. The ether left, on evaporation, a syrupy residue, which gradually deposited well-formed oblique prisms, which melted at 51° – 52° . The melting point of the substance, its characteristic crystalline form, and its reactions with alkalies and argentic nitrate, left little doubt that it was bromal hydrate, although the percentage of bromine which it gave on analysis was somewhat too low.

0.1351 gram substance gave 0.2534 gram AgBr.

	Calculated for $C_2Br_3H_3O_2$.	Found.
Br	80.26	79.84

We found that the purification of this substance by recrystallisation was attended with so great loss that we could hardly draw any definite conclusion as to the composition of the main product from analyses of the small purified residue, and we therefore determined to examine the products formed from it by the action of alkalies. Instead of extracting with ether the solution neutralised with calcic carbonate, we added to it a slight excess of potassic hydrate, and distilled, after neutralising the slightly alkaline solution with hydrochloric acid. In this way we obtained a colorless, heavy oil, which was easily recognised as bromoform. After drying over fused calcic chloride, it boiled at 147° – 150° , under a pressure of 748 mm. Its identity was further established by analysis.

I. 0.1739 gram substance gave 0.3893 gram AgBr.

II. 0.2202 gram substance gave 0.4940 gram AgBr.

	Calculated for $CHBr_3$.	Found.	
		I.	II.
Br	94.86	95.28	95.48

The weight of bromoform thus obtained amounted to between sixty and seventy per cent. of that required by the assumption that each molecule of the acid yielded one molecule of bromal.

The residue left after distilling off the bromoform was then acidified and distilled with steam. The acid distillate contained formic

acid, as was shown by the ordinary qualitative tests and by the analysis of the lead salt prepared from it.

0.3193 gram of the salt dried at 100° gave 0.3256 gram PbSO_4 .

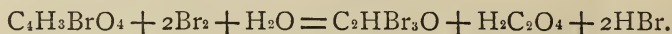
	Calculated for $\text{Pb}(\text{CHO}_2)_2$.	Found.
Pb	69.69	69.66

One of the products of the reaction was therefore bromal. In the insoluble residue removed by filtration after neutralising with calcic carbonate was found oxalic acid in abundance, which was identified by qualitative reactions and by the analysis of its calcium salt.

0.3779 gram of the salt dried at 100° gave 0.3490 gram CaSO_4 .

	Calculated for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.	Found.
Ca	27.39	27.16

The decomposition of mucoxybromic acid by aqueous bromine may therefore be expressed by the equation

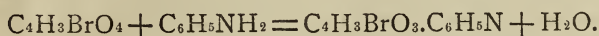


Although phenylhydrazine readily reacts upon mucoxybromic acid, even in dilute solution, the flocculent product formed rapidly turns brown, and we have not succeeded in obtaining it in a form fit for analysis. Hydroxylamine also yielded no more satisfactory results, although we tried the reaction under a variety of conditions. On the other hand, the primary aromatic amines in neutral or acid solutions gave beautifully crystalline products with the greatest readiness. Aniline, parabromaniline, para- and metanitraniline, ortho- and paratoluidine, all yielded similar products, but we have thus far studied in detail the aniline compound alone. Urea likewise gives a crystalline condensation product which has not yet been further investigated.

Anilmucoxybromic Acid.

When aniline chloride is added to a dilute solution of mucoxybromic acid, the solution soon becomes yellow, and after a short time solidifies, with the separation of finely felted, light yellow needles. A moderate excess of free hydrochloric acid in no way interferes with the formation of the product, so that it may be most conveniently prepared by dissolving baric mucoxybromate in a slight excess of dilute hydrochloric acid, and adding a mole-

cule of aniline dissolved in hydrochloric acid. The product was recrystallised from hot water, dried over sulphuric acid, and proved then to be anilmucoxybromic acid, formed according to the equation



I. 0.2775 gram substance gave 0.4540 gram CO_2 and 0.0790 gram H_2O .

II. 0.2602 gram substance gave 0.1810 gram AgBr.

III. 0.2526 gram substance gave 0.1764 gram AgBr.

IV. 0.5563 gram substance gave 25.2 cc. of moist nitrogen at 19° and under a pressure of 748 mm.

	Calculated for $\text{C}_{10}\text{H}_8\text{BrNO}_3$.	I.	Found. II.	III.	IV.
C	44.44	44.62			
H	2.96	3.16			
Br	29.63	...	29.61	29.73	
N	5.18	...	...	...	5.21

The air-dried acid apparently contained one molecule of water, which it lost rapidly over sulphuric acid or when heated to 70° . At 100° a slow decomposition appeared to take place. The loss of crystal water was accompanied by a change of color to brilliant yellow.

I. 0.5579 gram of air-dried substance lost, at 62° – 65° , 0.0362 gram H_2O .

II. 0.9504 gram of air-dried substance lost, at 70° , 0.0630 gram H_2O .

III. 1.0217 gram of air-dried substance lost over sulphuric acid 0.0786 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_8\text{BrNO}_3 \cdot \text{H}_2\text{O}$.	I.	Found. II.	III.
H_2O	6.25	6.49	6.63	7.69

Anilmucoxybromic acid crystallises from water in fine pale yellow needles, which are sparingly soluble in cold water, more readily in hot. On long heating of the aqueous solution decomposition sets in. The acid dissolves readily in alcohol, ether, or in hot chloroform or benzol; in ligroin or carbonic disulphide it is sparingly soluble. From chloroform it crystallises in small compact oblique prisms, which melt, with decomposition, at 131° – 132° . The acid dissolves readily in solutions of the alkaline carbonates, and is reprecipitated unchanged on the addition of acids. With the salts

of the heavy metals it gives brilliant yellow insoluble salts, and with ferric chloride it yields a deep brown precipitate. On heating with acids or alkalis, aniline is formed. On titration with baric hydrate two molecules of the acid were found to be neutralised by one molecule of baric hydrate, but salts containing two atoms of silver and potassium could also be prepared.

Monobaric Anilmucoxybromate, $\text{Ba}(\text{C}_{10}\text{H}_7\text{BrNO}_3)_{\frac{1}{2}}\cdot\frac{1}{2}\text{H}_2\text{O}$.—By the action of baric carbonate upon the acid suspended in water, a salt is formed which is somewhat sparingly soluble in hot or cold water. On evaporation of the solution a portion of the salt separates in yellow needles, but decomposition soon ensues. On the addition of baric acetate to the acid neutralised with ammoniac hydrate, an amorphous flocculent precipitate was thrown down, which dissolved on heating, and immediately in its place there appeared a highly crystalline bright yellow precipitate. As the solution cooled, still more of the salt separated in felted needles. The air-dried salt apparently contained a half-molecule of crystal water, which it lost at 100° .

0.5802 gram of the air-dried salt lost, at 100° , 0.0075 gram H_2O .

	Calculated for $\text{Ba}(\text{C}_{10}\text{H}_7\text{BrNO}_3)_{\frac{1}{2}}\cdot\frac{1}{2}\text{H}_2\text{O}$.	Found.
H_2O	1.32	1.25

0.5755 gram of this salt dried at 100° gave 0.1970 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_{10}\text{H}_7\text{BrNO}_3)_2$.	Found.
Ba	20.30	20.12

Diargentic Anilmucoxybromate, $\text{Ag}_2\text{C}_{10}\text{H}_6\text{BrNO}_3$.—When argentic nitrate was added to an aqueous solution of the free acid, a pale yellow gelatinous precipitate was thrown down, which apparently contained one atom of silver. If, however, the acid was dissolved in two equivalents of ammoniac hydrate, and the solution was then added to an excess of argentic nitrate, a voluminous bright orange-yellow precipitate was thrown down, which on standing became dense and semi-crystalline, and contained two atoms of silver. When warmed with an excess of argentic nitrate in a feebly ammoniacal solution, no immediate reduction took place.

0.4275 gram of the salt dried over H_2SO_4 gave 0.3290 gram AgBr .

	Calculated for $\text{Ag}_2\text{C}_{10}\text{H}_6\text{BrNO}_3$.	Found.
Ag	44.64	44.21

Dipotassic Anilmucoxybromate, $K_2C_{10}H_8BrNO_3$.—On the addition of an alcoholic solution of potassic hydrate to a solution of the acid in anhydrous ether, a pale yellow salt was thrown down, which was well washed with anhydrous ether, and dried in vacuo over sulphuric acid and solid sodic hydrate.

0.3556 gram of the salt gave 0.1805 gram K_2SO_4 .

Calculated for $K_2C_{10}H_8BrNO_3$.

22.58

Found.

22.79

While anilmucoxybromic acid forms by preference monobasic salts, it is evidently capable of exchanging two of its hydrogen atoms for metals.

Phenylhydrazine Anilmucoxybromate, $C_{10}H_8BrNO_3 \cdot C_6H_8N_2 \cdot H_2O$.—When phenylhydrazine hydrochlorate is added to anilmucoxybromic acid dissolved in a dilute solution of sodic acetate, a colorless crystalline precipitate soon separates, which, after washing with cold water, becomes somewhat discolored on drying. The compound is but sparingly soluble in cold water, more readily in hot, but it cannot be recrystallised from hot water without decomposition. It is readily soluble in alcohol, but nearly insoluble in ether. It is readily decomposed in the cold by dilute hydrochloric acid, or by a dilute solution of sodic carbonate, with the formation of phenylhydrazine. This behavior showed the substance to be a simple salt of phenylhydrazine, and analysis also failed to show the elimination of water.

0.3708 gram of the air-dried substance gave 36.5 cc. of moist nitrogen at 25° under a pressure of 726 mm.

Calculated for $C_{16}H_{16}BrN_3O_3 \cdot H_2O$.

N

10.60

Found.

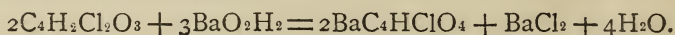
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Mucoxychloric Acid.

W. Z. Bennett¹ and one of us several years ago studied the action of baric hydrate upon mucochloric acid. It was found that the acid was decomposed by a large excess of baric hydrate, and that $\alpha\beta$ dichloracrylic and formic acids were formed in nearly theoretical quantities. When the baric hydrate is carefully added, so that the solution is at no time very strongly alkaline, the reaction follows an entirely different course, and mucoxychloric acid is found in abundance. Since the $\alpha\beta$ dichloracrylic acid had already

¹ Proceedings American Academy 16, 206.

been shown to be more stable than the corresponding dibrom-acrylic acid, we were led to study mucoxychloric acid more in detail, with the hope that its derivatives would also prove more stable and more manageable than those of mucoxybromic acid. In the preparation of mucoxychloric acid we followed precisely the same method which we had found advantageous with the bromine compound. Mucochloric acid¹ was suspended in 35 times its weight of water, and, after cooling well with ice, the theoretical quantity of finely powdered baric hydrate was slowly added, taking care to avoid at any time a large excess. After the requisite amount of baric hydrate had been added, we allowed the solution to stand over night, and removed the slight excess of baric hydrate, which was then usually found present, by means of carbonic dioxide. The filtered solution gave, when mixed with an equal volume of alcohol, a voluminous highly crystalline precipitate of baric mucoxychlorate, which could be purified by reprecipitation from aqueous solution by alcohol. In this way we have obtained 73 per cent. of the theoretical amount of barium salt demanded by the equation



The mother liquors contain, beside baric chloride, baric $\alpha\beta$ dichloracrylate, which may be obtained without difficulty by the evaporation of the solution. Although ether extracts the acid

¹ Although W. Z. Bennett and I had succeeded in obtaining a fairly satisfactory yield of mucochloric acid, the method which we used was troublesome and tedious in the extreme when large quantities of material were involved, and necessitated the prolonged treatment of large quantities of liquid at 0° with chlorine gas. The slightest want of care also frequently diminished the yield most seriously. I therefore made many fruitless attempts to find some more advantageous method for its preparation. I at last hit upon an extremely convenient and simple method, which allows the preparation of any quantity of mucochloric acid desired in the course of a few hours. The yield is also quite satisfactory, and falls not far short of that which is attainable by the old method. Pyromucic acid is suspended in 14½ times its weight of common strong hydrochloric acid (sp. gr. 1.16), and somewhat more than four molecules of finely powdered manganic dioxide are then gradually added. At first the mixture is kept cold (ice cooling is unnecessary). The temperature is then allowed to rise, and finally the solution is heated and boiled gently for twenty minutes. Since it is difficult to filter the hot strongly acid liquid from the impurities contained in the manganic dioxide, the solution is allowed to cool, and the mucochloric acid which separates collected upon a filter of coarse cloth. It is then dissolved in hot water, and the filtered solution concentrated by evaporation if necessary. From 100 grams of pyromucic acid suspended in 1250 cc. of ordinary hydrochloric acid and 380 grams of manganese dioxide (83 per cent. MnO_2), 50 grams of pure mucochloric acid are readily obtained, and the mother liquors yield 2-3 grams of a somewhat dark-colored acid. Bennett and I obtained by the much more laborious method, as the result of many separate operations, 129 grams of mucochloric acid from 202 grams pyromucic acid. This method accordingly yields in a short time about 83 per cent. of the amount attainable by the more tedious method.

—H. B. H.

from aqueous solution, it does not take it up very readily, and we have found it more advantageous to precipitate the barium salt exactly with dilute sulphuric acid, and evaporate the aqueous solution thus obtained in vacuo over sulphuric acid. The acid may readily be recrystallised with care from a little warm water. For analysis the acid was dried over sulphuric acid.

I. 0.2925 gram substance gave 0.3420 gram CO_2 and 0.0615 gram H_2O .

II. 0.1990 gram substance gave 0.1915 gram AgCl .

III. 0.2000 gram substance gave 0.1918 gram AgCl .

	Calculated for $\text{C}_4\text{H}_3\text{ClO}_4$.	I.	Found. II.	III.
C	31.89	31.88		
H	1.99	2.33		
Cl	23.59	...	23.79	23.71

Mucoxychloric acid is readily soluble in water, alcohol, or ether, and almost insoluble in chloroform, benzol, ligroin, or carbonic disulphide. From water it crystallises in stout prisms with beveled ends, which melt at 114° – 115° . With ferric chloride it gives, even in extremely dilute solutions, a deep garnet-red coloration. With argentic nitrate it gives an immediate crystalline precipitate of the silver salt. Although more stable than mucoxybromic acid, it is soon decomposed by warming its aqueous solution.

Baric Mucoxychlorate, $\text{BaC}_4\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.—The preparation of the barium salt has already been described. It is sparingly soluble in cold water, more readily in hot, and is nearly insoluble in dilute alcohol. Although it is decomposed by heating its aqueous solution, the decomposition is not particularly rapid, and small quantities of the salt may be recrystallised from hot water with little difficulty. It crystallises then in fine clustered needles, and is obtained in the same form by precipitating its aqueous solution with alcohol. In evaporating a cold aqueous solution in vacuo over sulphuric acid, the salt may be obtained in long lustrous prisms with perpendicular terminations. The salt crystallised from water, or precipitated by alcohol, when air-dried, loses over sulphuric acid somewhat more than one molecule of water, and has then the composition $\text{BaC}_4\text{HClO}_4 \cdot \text{H}_2\text{O}$.

I. 2.5352 grams of salt recrystallised from water and dried by exposure to the air lost over sulphuric acid 0.1706 gram H_2O .

II. 2.2127 grams of salt recrystallised from water and dried by exposure to the air lost over sulphuric acid 0.1480 gram H_2O .

III. 1.9160 grams of salt precipitated by alcohol and dried by exposure to the air lost over sulphuric acid 0.1288 gram H_2O .

IV. 1.5273 grams of salt precipitated by alcohol and dried by exposure to the air lost over sulphuric acid 0.1054 gram H_2O .

	Calculated for $\text{BaC}_4\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.	I.	II.	Found, III.	IV.
H_2O	5.60	6.73	6.69	6.73	6.90

The salt dried over sulphuric acid contained a percentage of barium agreeing closely with that required by the formula $\text{BaC}_4\text{HClO}_4 \cdot \text{H}_2\text{O}$. It lost weight slowly at 100° – 105° , but only the compact salt crystallised from water could be brought to constant weight at this temperature without essential decomposition. The voluminous salt precipitated by alcohol after many weeks still lost in weight, contained baric chloride, and had become badly discolored.

I. 1.4644 grams of salt recrystallised from water and dried over sulphuric acid lost, at 100° – 105° , 0.0820 gram H_2O .

II. 1.4771 grams of salt recrystallised from water and dried over sulphuric acid lost, at 100° – 105° , 0.0827 gram H_2O .

III. 0.8947 gram of salt recrystallised from water and dried over sulphuric acid gave 0.6871 gram BaSO_4 .

IV. 0.5865 gram of salt recrystallised from water and dried over sulphuric acid gave 0.4498 gram BaSO_4 .

V. 0.3261 gram of salt precipitated by alcohol and dried over sulphuric acid gave 0.3266 gram BaSO_4 .

	Calculated for $\text{BaC}_4\text{HClO}_4 \cdot \text{H}_2\text{O}$.	I.	II.	Found, III.	IV.	V.
H_2O	5.93	5.60	5.60			
Ba	45.14	...	...	45.16	45.08	45.06

Although the crystallised baric mucoxychlorate suffers no change when exposed to the air for a week or more, after months of exposure it loses in weight and the clear prismatic crystals become opaque. The salt is then more sparingly soluble in water, and crystallises in small oblique prisms. These same oblique crystals are also occasionally deposited together with the long rectangular prisms on evaporating in vacuo the aqueous solution of the salt originally obtained. An analysis showed that these oblique prisms contained a percentage of barium required by a salt crystallising with one molecule of water. Although the crystalline form appeared to be persistent, we were able to detect no

differences in the chemical behavior of the salt, or of the acid prepared from it, which would warrant the assumption that any radical change in its structure had taken place.

For analysis, the oblique prisms were well washed with cold water and dried by exposure to the air. The air-dried salt lost nothing over sulphuric acid, and lost weight but slowly at 100°.

0.4076 gram of air-dried salt gave 0.3131 gram BaSO_4 .

	Calculated for $\text{BaC}_4\text{HClO}_4 \cdot \text{H}_2\text{O}$.	Found.
Ba	45.14	45.15

Potassic Mucoxychlorate, $\text{K}_2\text{C}_4\text{HClO}_4$.—The potassium salt we prepared by decomposing the barium salt with potassic carbonate and evaporating the filtered solution in vacuo over sulphuric acid. The salt separated in small tabular crystals, which were recrystallised from warm water. The air-dried salt lost nothing when heated at 100°.

I. 0.4344 gram of the salt gave 0.3334 gram K_2SO_4 .

II. 0.4631 gram of the salt gave 0.3547 gram K_2SO_4 .

	Calculated for $\text{K}_2\text{C}_4\text{HClO}_4$.	I.	Found.	II.
K	34.49	34.45		34.39

Argentio Mucoxychlorate, $\text{Ag}_2\text{C}_4\text{HClO}_4$.—The silver salt was made by precipitating a solution of argentic nitrate with a solution of the potassium salt. On heating, argentic chloride was rapidly formed. On warming with a little ammoniac hydrate, immediate reduction ensued. From a solution of the free acid, argentic nitrate threw down the neutral salt (III).

I. 0.5024 gram of the salt dried over H_2SO_4 gave 0.3948 gram AgCl .

II. 0.4125 gram of the salt dried over H_2SO_4 gave 0.3240 gram AgCl .

III. 0.3704 gram of the salt dried over H_2SO_4 gave 0.2891 gram AgCl .

	Calculated for $\text{Ag}_2\text{C}_4\text{HClO}_4$.	I.	Found.	III.
Ag	59.27	59.17	59.13	58.76

Diethyl Mucoxychlorate, $\text{C}_4\text{HClO}_4(\text{C}_2\text{H}_5)_2$.—Finely powdered argentic mucoxychlorate, which had been well dried over sulphuric acid, was gradually thrown into an excess of ethyl iodide. The heat evolved by the reaction was so great that the boiling point of the ethyl iodide was soon reached, and the decomposition was

afterward completed by heating for a short time on the water-bath. The product of the reaction was then extracted by dry chloroform, the chloroform distilled off under diminished pressure, and the viscous residue placed over sulphuric acid in vacuo. After long standing in vacuo the product showed no signs of crystallisation, but proved to contain a percentage of chlorine which agreed tolerably well with that required by the diethyl ether.

0.2314 gram substance gave 0.1553 gram AgCl.

	Calculated for $C_4H_2ClO_4(C_2H_5)_2$.	Found.
Cl	17.19	16.59

Monoethyl Mucoxychlorate, $C_4H_2ClO_4.C_2H_5$.—When the viscous diethyl ether just described was allowed to stand exposed to the air, or when it was mixed with a small quantity of water, it rapidly acquired an acid reaction, and gradually deposited well-formed crystals of the monoethyl ether. The latter could also readily be prepared by extracting with ordinary aqueous ether the product formed by the action of ethyl iodide upon the silver salt, and allowing the ethereal solution to evaporate spontaneously. The crystals which separated were thoroughly pressed and recrystallised from boiling benzol.

I. 0.2337 gram substance gave 0.3445 gram CO_2 and 0.0870 gram H_2O .

II. 0.2659 gram substance gave 0.2147 gram AgCl.

III. 0.2572 gram substance gave 0.2080 gram AgCl.

	Calculated for $C_4H_2ClO_4.C_2H_5$.	I.	Found. II.	III.
C	40.33	40.20		
H	3.92	4.13		
Cl	19.89	...	19.95	20.00

Monoethyl mucoxychlorate crystallises in clustered, obliquely truncated prisms, which melt at 94° – 95° , and sublime unchanged at higher temperature. It dissolves readily in water, alcohol, ether, or chloroform, quite readily in boiling benzol, more sparingly in cold, and but sparingly in ligroin. Its aqueous solution is strongly acid to litmus, dissolves carbonates with effervescence, and gives a deep red coloration with ferric chloride. When baric hydrate is slowly added to the aqueous solution, a yellow color is developed, and products formed which we have not yet more fully studied. If, however, the ether is dissolved in an excess of baric hydrate, it is saponified and baric mucoxychlorate formed. The alkaline

solution was precipitated with carbonic dioxide, and alcohol added to the filtered solution. The crystalline salt which separated was dissolved in cold water, and the solution evaporated over sulphuric acid in vacuo.

0.7070 gram of air-dried salt lost over sulphuric acid 0.0482 gram H_2O .

	Calculated for $\text{BaC}_4\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.	Found.
H_2O	5.60	6.82

0.6588 gram of the salt dried over H_2SO_4 lost, at 100° , 0.0385 gram H_2O .

	Calculated for $\text{BaC}_4\text{HCl} \cdot \text{H}_2\text{O}$.	Found.
H_2O	5.93	5.85

0.6203 gram of the salt dried at 100° gave 0.3535 gram BaSO_4 .

	Calculated for $\text{BaC}_4\text{HClO}_4$.	Found.
Ba	47.98	47.85

Decomposition in Alkaline Solution.

The instability of mucoxychloric acid and its salts when heated in aqueous solution has already been mentioned. We have, however, as yet studied more closely only the reaction which takes place when baric mucoxychlorate is heated with an excess of baric hydrate. The solution soon grows turbid on boiling, and throws down baric oxalate and baric carbonate, while the solution then contains baric chloride and formiate. The insoluble salts were collected upon a filter, and the presence of carbonic and oxalic acids established by qualitative tests. The presence of oxalic acid was still further confirmed by an analysis of the calcium salt.

0.1740 gram of the salt dried at 100° gave 0.1608 gram CaSO_4 .

	Calculated for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.	Found.
Ca	27.39	27.17

The aqueous solution filtered from the insoluble salts was freed from the excess of baric hydrate by means of carbonic dioxide. It gave then with argentic nitrate an abundant precipitate of argentic chloride, and blackened when heated with an excess of argentic nitrate. The barium was removed by dilute sulphuric acid, and the filtered solution distilled. The acid distillate when neutralised with plumbic carbonate yielded plumbic formiate in characteristic form.

0.3244 gram of the salt dried at 100° gave 0.3327 gram PbSO_4 .

	Calculated for $\text{Pb}(\text{CHO}_2)_2$.	Found.
Pb	69.69	70.06

As was the case with the corresponding decomposition of mucoxybromic acid, quantitative determinations of the amounts of oxalic and carbonic acid formed in the reaction showed no simple relation between the two, and at the same time products were formed in small but significant amounts, whose nature we have as yet been unable to determine.

Action of Bromine in Aqueous Solution.

Bromine acts readily upon an aqueous solution of mucoxychloric acid, and forms products strictly analogous to those formed from mucoxybromic acid under the same conditions. Since the chlorobromal hydrate proved to be even less manageable than the bromal hydrate, we thought it best to determine its presence, as before, from its decomposition products. Since the reaction seemed to be quite as neat with the salts as with the free acid, we added to a diluted aqueous solution of the barium salt two molecules of bromine, and allowed the mixture to stand at ordinary temperatures until the color of the bromine had completely disappeared. We then neutralised the strongly acid solution with calcic carbonate in the cold, and filtered. The insoluble residue thus obtained contained oxalic acid in abundance, and we were unable to detect in it any other organic constituent. The oxalic acid was converted into its calcium salt and analysed.

0.3489 gram of the salt dried at 100° gave 0.3212 gram CaSO_4 .

	Calculated for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.	Found.
Ca	27.39	27.08

To the clear aqueous solution we added a slight excess of potassic hydrate, neutralised after a short time with hydrochloric acid, and distilled the neutral solution with steam. We obtained in this way a colorless heavy oil, which, when dried with calcic chloride, boiled without decomposition at 119° – 120° under a pressure of 748 mm.¹ Analysis showed it to be dibromchlormethan.

I. 0.1545 gram substance gave 0.3855 gram $\text{AgCl} + \text{AgBr}$.

II. 0.1418 gram substance gave 0.3536 gram $\text{AgCl} + \text{AgBr}$.

	Calculated for CHClBr_2 .	I. Found.	II.
$\text{Cl} + \text{Br}$	93.74	93.91	93.85

The weight of dibromchlormethan thus obtained was about sixty per cent. of the theoretical amount.

¹ According to O. Jacobsen and R. Neumeister (Ber. d. deutsch. chem. Gesellsch. **15**, 601), chlorobromoform boils between 123° and 125° , with slight decomposition.

The residue left after distillation was acidified, and again distilled with steam. The acid distillate thus obtained was neutralised with plumbic carbonate, and yielded upon evaporation plumbic formiate.

0.3936 gram of the salt dried at 100° gave 0.4003 gram PbSO_4 .

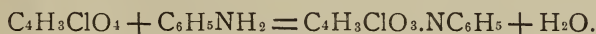
	Calculated for $\text{Pb}_2(\text{CHO}_2)_2$.	Found.
Pb	69.69	69.47

The decomposition of mucoxychloric acid by aqueous bromine may therefore be expressed by the equation



Anilmucoxychloric Acid.

Mucoxychloric acid, like mucoxybromic acid, readily gives with phenylhydrazine a condensation product. It has, however, little stability, and we have therefore not studied it more closely. With aniline, however, it gives even in dilute acid solutions a beautifully crystalline product. For its preparation we added one molecule of aniline hydrochlorate to a solution of the barium salt in a slight excess of dilute hydrochloric acid. The solution soon turned yellow, and after standing for a short time solidified with the separation of pale yellow finely felted needles. At low temperatures the crystals formed were often nearly colorless. When recrystallised from hot water and dried over sulphuric acid, the substance was shown by analysis to be anilmucoxychloric acid formed according to the equation



I. 0.2146 gram substance gave 0.4170 gram CO_2 and 0.0791 gram H_2O .

II. 0.1797 gram substance gave 0.1142 gram AgCl .

III. 0.1865 gram substance gave 0.1186 gram AgCl .

IV. 1.0389 gram substance gave 60.6 cc. moist nitrogen at 23° and under a pressure of 746 mm.

	Calculated for $\text{C}_{10}\text{H}_5\text{ClNO}_3$.	I.	II.	Found.	III.	IV.
C	53.21	52.99				
H	3.54	4.10				
Cl	15.74	...	15.71	15.72		
N	6.21	...	...	...		6.60

The air-dried acid apparently contains one molecule of water of crystallisation, which it loses readily over sulphuric acid or when

heated to 100° . With the loss of water the pale yellow or almost colorless needles become brilliant yellow.

I. 0.7579 gram of air-dried acid lost, at 100° , 0.0597 gram H_2O .

II. 0.9022 gram of air-dried acid lost, at 100° , 0.0702 gram H_2O .

III. 0.5646 gram of air-dried acid lost over H_2SO_4 0.0460 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_7\text{ClNO}_2$.	I.	Found. II.	III.
H_2O	7.39	7.88	7.78	8.15

Anilmucoxychloric acid is sparingly soluble in cold water, more readily in hot, and appears to suffer slow decomposition when its aqueous solution is boiled. It dissolves readily in alcohol or ether, sparingly in cold benzol or chloroform, more freely on heating. In ligroin or carbonic disulphide it is nearly insoluble. From chloroform it crystallises in small compact oblique prisms, which melt with decomposition at 145° – 147° . The acid dissolves readily in solutions of the alkaline carbonates, and is reprecipitated unchanged by the addition of acids. In heating with acids or alkalis aniline is formed. An aqueous solution of the free acids gives deep yellow precipitates with salts of most of the heavy metals. With ferric chloride it gives a deep brown precipitate. It forms by preference monobasic salts, but we have prepared also dibasic salts.

Baric Anilmucoxychlorate, $\text{Ba}(\text{C}_{10}\text{H}_7\text{ClNO}_2)_{\frac{1}{2}}\text{H}_2\text{O}$.—If baric carbonate is added to anilmucoxychloric acid suspended in cold water, carbonic dioxide is disengaged, and a barium salt readily soluble in water is formed. If the concentrated filtered solution is then heated nearly to boiling, it soon deposits abundant bright yellow clustered needles, which increase somewhat in quantity as the solution cools. The air-dried salt lost slightly in weight at 100° . This loss corresponded to about one half-molecule of crystal water; it is possible, however, that it was hygroscopic moisture alone.

I. 0.2819 gram of the air-dried salt lost, at 100° , 0.0052 gram H_2O .

II. 0.9735 gram of the air-dried salt lost, at 100° , 0.0196 gram H_2O .

	Calculated for $\text{Ba}(\text{C}_{10}\text{H}_7\text{ClNO}_2)_{\frac{1}{2}}\text{H}_2\text{O}$:	I.	Found. II.
H_2O	1.51	1.85	2.01

I. 0.2767 gram of the salt dried at 100° gave 0.1102 gram BaSO_4 .

II. 0.3918 gram of the salt dried at 100° gave 0.1561 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_{10}\text{H}_7\text{ClNO}_3)_2$.	I.	Found.	II.
Ba	23.37	23.42		23.42

Diargentic Anilmucoxychlorate, $\text{Ag}_2\text{C}_{10}\text{H}_6\text{ClNO}_3$.—When argentic nitrate is added to a cold aqueous solution of anilmucoxychloric acid, a pale yellow gelatinous precipitate is formed, which is hard to wash and prepare for analysis, and doubtless contains one atom of silver. If, however, the acid is dissolved in two equivalents of dilute ammoniac hydrate, and this solution poured into an excess of argentic nitrate, a bright orange-yellow flocculent precipitate is thrown down, which becomes more compact on standing, and contains two atoms of silver. This salt showed but slight discoloration when warmed for some time with an excess of argentic nitrate in a feebly ammoniacal solution.

0.5431 gram of the salt dried over H_2SO_4 gave 0.3516 gram AgCl .

	Calculated for $\text{Ag}_2\text{C}_{10}\text{H}_6\text{ClNO}_3$.	Found.
Ag	49.15	48.73

Dipotassic Anilmucoxychlorate, $\text{K}_2\text{C}_{10}\text{H}_6\text{ClNO}_3$.—When an alcoholic solution of potassic hydrate was added, in slight excess, to a solution of anilmucoxychloric acid in dry ether, a pale yellow salt was precipitated, which when dried in vacuo over sulphuric acid and powdered sodic hydrate proved to contain two atoms of potassium.

0.6070 gram of the salt gave 0.3579 gram K_2SO_4 .

	Calculated for $\text{K}_2\text{C}_{10}\text{H}_6\text{ClNO}_3$.	Found.
K	25.92	26.47

Phenylhydrazine Anilmucoxychlorate, $\text{C}_{10}\text{H}_8\text{ClNO}_3 \cdot \text{C}_6\text{H}_5\text{N}_2 \cdot \text{H}_2\text{O}$.—When phenylhydrazine hydrochlorate is added to anilmucoxychloric acid dissolved in a dilute solution of sodic acetate, a white crystalline substance soon separates, which becomes somewhat discolored on drying. It is sparingly soluble in cold water, readily soluble in alcohol, but insoluble in ether. It is decomposed in the cold by dilute hydrochloric acid, or by a dilute solution of sodic carbonate, with the formation of phenylhydrazine. This behavior shows that it is simply a salt of phenylhydrazine rather than a characteristic condensation product. The substance was well washed with cold water and dried over sulphuric acid.

I. 0.3000 gram substance gave 0.1189 gram AgCl.

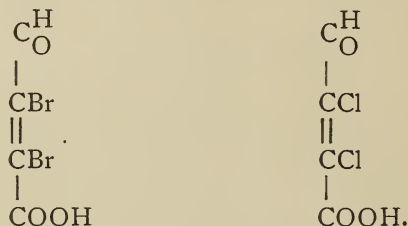
II. 0.3218 gram substance gave 34 cc. of moist nitrogen at 18° and under a pressure of 748 mm.

III. 0.2248 gram substance gave 23.5 cc. moist nitrogen at 20° and under a pressure of 741 mm.

	Calculated for $C_{16}H_{16}ClN_3O_2.H_2O$.	I.	Found. II.	III.
Cl	9.98	9.80		
N	11.81	...	12.20	11.87

THEORETICAL CONSIDERATIONS.

Although the facts which we have observed are in certain respects difficult of interpretation, it seems to us that, on the whole, they warrant tolerably definite conclusions as to the constitution of mucoxybromic and mucoxychloric acids. We may safely assume that mucobromic and mucochloric acids are to be represented by the formulæ¹

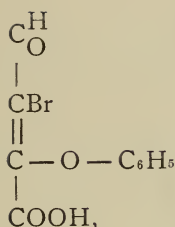


It is evident that the carboxyl group is not affected by the reaction in question, and, furthermore, that the aldehyde group is also still contained in the mucoxybromic and mucoxychloric acids. The latter fact is sufficiently proved by the behavior of the two acids with argentic nitrate, by the ready formation of condensation products with aniline, and, lastly, by the appearance of substituted aldehydes among the products formed from them by the action of aqueous bromine. The two central carbon atoms are therefore alone concerned in the transformation of mucobromic and mucochloric acids into the corresponding oxy-acids; and the first steps at least in this change must be the replacement of one of the halogen atoms by hydroxyl.

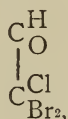
Since potassic phenylate acts upon mucobromic acid with the formation of mucophenoxybromic acid, whose constitution has been shown to be²

¹ Proceedings American Academy 16, 218; 17, 150.

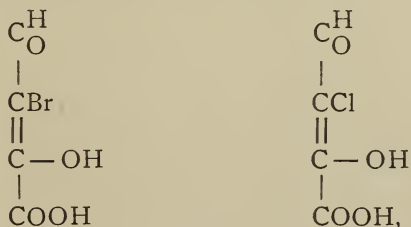
² This Journal 6, 194; and Proceedings American Academy 19, 268.



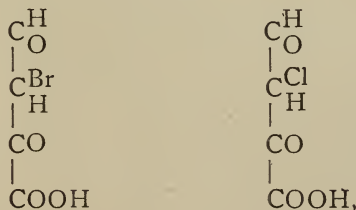
it could safely be assumed that in the analogous reaction with baric hydrate the α -halogen atom would also be first replaced. The formation of dibromchlor aldehyde,



by the action of bromine upon mucoxychloric acid, proves that this assumption is correct, since the β -chlorine atom has here retained its place. It follows, therefore, that the mucoxybromic and mucoxychloric acids are either hydroxyl acids formed by the replacement of the α -halogen atoms by hydroxyl,



or that they are the ketone acids,

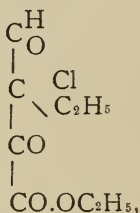
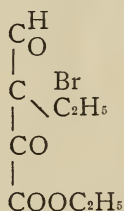


formed from them by the ordinarily observed molecular rearrangement.

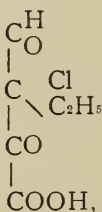
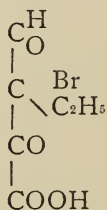
While a satisfactory explanation of the persistent dibasic character

of the two acids can hardly be found in these formulæ, the formation of dibasic salts from either cannot be pronounced impossible, and no definite argument in favor of either formula can be based upon this behavior.

The ready and complete saponification of the ether of the two acids with the formation of the original dibasic metallic salts seems on the other hand an insurmountable objection to the ketone formula. The diethyl ethers of the ketone acids,



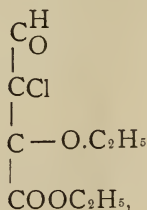
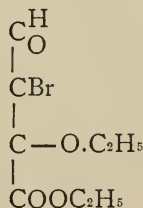
must of necessity yield upon saponification homologous monobasic acids,



unless indeed a complete destruction of the molecule ensues.

We are therefore unable to resist the conclusion that mucoxybromic and mucoxychloric acids contain hydroxyl—that they are in fact phenol acids of the paraffine series, in which the hydroxyl has strongly marked acid properties on account of its peculiar environment.

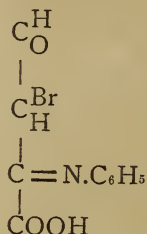
The anomalous removal of the ethyl groups from the ethers,



by saponification with baric hydrate, seems to us to be conditioned



That the dibasic character of these compounds has been impaired by the introduction of the aniline residue is but natural, while the persistence of this dibasic character shows that they cannot be derived from the ketone formula by the replacement of the ketone oxygen. A compound of the form



could hardly form dibasic salts.

Moreover, the fact that these aniline derivatives do not form stable condensation products with phenylhydrazine may be taken as further evidence that they contain hydroxyl, and not the ketone or aldehyde group. That we have not yet been able to reverse the reaction, and replace the hydroxyl groups again by the halogens, we cannot but think due simply to the instability of the acids themselves.

While we feel that the constitution of mucoxybromic and mucoxy-chloric acids is thus determined with reasonable certainty, further investigations upon the subject will be made in this laboratory.
